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(54) Title: IMPROVEMENTS RELATING TO SURFACTANT-OIL MICROEMULSION CONCENTRATES			
(57) Abstract			
<p>The disclosure relates to an aqueous cleaning composition which upon aqueous dilution by a factor of at least two produces a stable emulsion, said emulsion having a measured dispersed phase particle size of 10-100 nanometers, said composition including: a) 20-70 wt.% water, b) from 15-40 wt.% of a surfactant system comprising at least one alkoxylated alcohol nonionic surfactant and not more than 20 wt.% on surfactant of anionic, cationic, amphoteric or zwitterionic surfactant, c) from 5-30 wt.% of a solvent, said solvent having a solubility of greater than 2 % w/w but less than 12 % w/w in water, and d) 5-20 wt.% of a substantially water-insoluble oil, said composition having a measured dispersed phase particle size of greater than 100 nm prior to dilution. Advantageously, the compositions according to the invention are of relatively high viscosity and exhibit the property of clinging to a sloping surface, while, on dilution, they form mobile microemulsions.</p>			
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IMPROVEMENTS RELATING TO SURFACTANT-OIL
MICROEMULSION CONCENTRATES

5

Technical Field

The present invention relates to surfactant-oil
microemulsion concentrates, especially those suitable for
10 use both neat and diluted as cleaning compositions, and to
a method of cleaning using the said concentrates.

Background of the Invention

15

Aqueous cleaning compositions generally comprise at least
one surfactant component. Many known cleaning
compositions further comprise water-immiscible components,
such as oils, fatty alcohols and/or terpenes. It is known
20 that systems comprising a surfactant, water and these
water immiscible components can assume different phase
structures.

Three types of phase which comprise surfactant and water
25 are generally recognised: the rod-phase, the lamellar
phase and the spherical micellar phase.

In the spherical phase, surfactant molecules align in
spheres having a diameter approximately twice the
30 molecular length. For anionic actives in common use,
these structures are less than 10nm in diameter. Systems
exhibiting this phase structure are clear, have a
viscosity similar to water and cannot suspend particles.

35 The rod phase can be considered as a spherical phase which
has been encouraged to grow along one dimension. It is

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known that this can be achieved by the addition of oils. Typically, the rods grow to relatively large length as compared with the diameter, resulting in highly viscous, often opaque solutions. Although the viscosity of these systems is relatively high as compared with spherical micellar solutions, any suspended particles will eventually phase separate.

The lamellar phase is believed to be characterised by the presence of extensive bi-layers of aligned surfactant molecules separated by water layers. These systems are generally of lower viscosity than the rod phase systems, are often opaque and can suspend particles.

When an oil is added to a surfactant-water system the oil can remain in a separate phase or form part of a mixed phase. The so-called 'microemulsions' are believed to be oil-in-water emulsions wherein the oil droplets are sufficiently small that a visibly clear system results.

For the purposes of the present invention, the term 'microemulsion' is restricted to those systems in which particle size measurements reveal a particle size range of 10-100nm. These systems have a low viscosity and will not suspend particles, but differ from spherical micelles in that they exhibit low interfacial tensions in the presence of other oily materials such as are common in fatty soils.

It is believed that the low interfacial tension enables the microemulsions to spontaneously emulsify such oily materials, giving a contribution towards a particular cleaning benefit as compared with spherical micelles.

As will be appreciated, microemulsions have a similar overall composition to the rod micellar systems which can be obtained by adding oil to a spherical micellar system

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but have a completely different phase structure and distinct physical properties. It is believed that in the microemulsions the oil phase is segregated into discrete droplets stabilised by a surfactant shell whereas in the
5 rod phase, the oil phase is mixed with the surfactant to form a mixed micellar structure.

For environmental reasons and for convenience to the user it is preferred that liquid surfactant compositions should
10 be as concentrated as is convenient given the mode of use. This not only reduces the energy cost in transport but also reduces the packaging requirement for a given quantity of product.

15 GB 2190681 (Colgate: 1987) and EP 316726 (Colgate: 1987) relate to systems which comprise both anionic and nonionic surfactant, together with a cosurfactant, a water-immiscible hydrocarbon such as an oily perfume and water. Surfactants may comprise solely anionic surfactants
20 although mixtures of anionics and nonionics are preferred. According to these texts, (see page 5, lines 31ff. of the GB specification) the cosurfactant is essential in that in the absence of this component the surfactants and the hydrocarbon will form a non-microemulsion phase structure.
25 Suitable cosurfactants are said to include glycol ether solvents such as Butyl Carbitol (RTM) which is miscible with water and Butyl Cellosolve (RTM) which is highly water soluble. These systems are very sensitive to the type of surfactant present and it appears difficult to
30 reproduce these systems without using the precise components specified.

GB 2144763 (P&G: 1983) relates to microemulsion systems which contain magnesium salts. Examples demonstrate that
35 aqueous liquid compositions can be prepared with anionic

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surfactants alone and with mixtures of anionic and nonionic surfactants.

5 US 4511488 (Penetone: 1985) relates to compositions which are described as clear, flowable compositions and which comprise 10-60wt% of d-limonene (a citrus oil), 10-30wt% surfactant, and, 20-70wt% water, in the presence of a coupling agent such as a glycol ether solvent, in particular Butyl Carbitol. It has been found by
10 experiment that high nonionic compositions such as are described in example 7 of this patent are not stable and phase separate rapidly on standing both in neat form and at x4 dilution.

15 From the above it can be seen that microemulsions generally comprise water, a surfactant mixture, an oil and a solvent. The surfactants are typically mixtures of anionic and nonionic surfactant. The oil is generally a perfume oil. The solvent is often referred to as a
20 'cosurfactant' or a 'coupling agent' and is generally a glycol ether.

Brief Description of the Invention

25 We have determined that stable, concentrated microemulsions can be prepared, by simultaneous selection of specific surfactants, specific oils and specific solvents. While these compositions are not microemulsions as defined herein, they are dilutable to give a stable
30 microemulsion which exhibits excellent fatty soil removal. For the purposes of the present specification a concentrated microemulsion is a composition which can be diluted with water to produce a microemulsion as defined
35 above.

- 5 -

Accordingly, the present invention provides an aqueous cleaning composition which upon aqueous dilution by a factor of at least two produces a stable emulsion, said emulsion having a measured dispersed phase particle size of 10-100 nanometeres, said composition including:

- a) 20-70wt% water,
 - b) from 15-40wt% of a surfactant system comprising at least one alkoxylated alcohol nonionic surfactant and not more than 20wt% on surfactant of anionic, cationic, amphoteric or zwitterionic surfactant,
 - c) from 5-30wt% of a solvent, said solvent having a solubility of greater than 2%w/w but less than 12%w/w in water, and,
 - d) 5-20wt% of a substantially water-insoluble oil,
- said composition having a measured dispersed phase particle size of greater than 100nm prior to dilution.

Advantageously the compositions according to the invention are of relatively high viscosity and exhibit the property of clinging to a sloping surface, while, on dilution, they form mobile microemulsions.

Detailed Description of the Invention

It is believed that the combined use of the specified level of nonionic surfactant in the presence of low levels of charged surfactant or even in the complete absence of charged surfactant, together with the specified levels of relatively insoluble solvent and less than 20% of a water-insoluble oil, in a composition with the required particle

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size; leads to the formulation of a viscous concentrate which is dilutable to give a microemulsion which exhibits improved fatty soil removal when compared with known compositions which contain conventional levels of anionic or which employ higher levels of solvent and or oil. We have also determined that neat compositions according to the invention show excellent cleaning performance and cling to sloping surfaces.

10 The compositions of the present invention, in their undiluted form, generally exhibit the property of bi-refringence, thereby indicating that a lamellar phase structure is present. Upon dilution, the bi-refrangent property is lost, indicating that the lamellar phase
15 structure is no longer present.

In many applications it is important that a composition should form a microemulsion over a range of dilution. In particular, if dilution takes the composition into a rod
20 phase it is possible that the resulting increase in viscosity will hinder further dilution. Moreover, if dilution takes the composition into the spherical phase the advantages of a microemulsion are lost, especially if physical separation of the oil phase occurs. Preferred
25 compositions according to the present invention form microemulsions when diluted with water to any dilution in the range x2-x16.

It is believed essential that the compositions of the
30 present invention have a particle size of above 100nm in the neat (i.e. concentrated) form. As mentioned above microemulsions are characterised by a measured particle size of 10-100 nm. In general the products of the present invention will be viscous liquids or gels which dilute to
35 thin liquids on addition of at least an equal volume of water. As indicated by the bi-refringence and viscosity

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it is believed that the compositions according to the invention are not microemulsions in their neat form.

5 The invention also extends to a process for cleaning a surface which comprises the step of treating the surface with a composition according to claim 1.

Surfactants

10

It is essential that the compositions of the invention comprise alkoxyated alcohol nonionic surfactant.

15

Suitable alkoxyated alcohol nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature.

20

The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

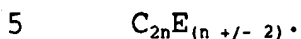
25

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a fatty alcohol ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of fatty alcohol. A plurality of such materials are described in Schick, 'Nonionic Surfactants', [pub. Arnold, New York].

35

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Particularly preferred nonionic surfactants are those wherein the average composition conforms to the general formula:



Particularly preferred surfactants include the $C_{8-13}E_{4-8}$ (average) alcohol ethoxylates. Examples of these materials include IMBENTIN 91-35 OFA (RTM) and DOBANOL 23-
10 6.5 (RTM).

Alternatives include the condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol. The
15 alkyl nonionics are preferred over the alkylphenyl nonionics for environmental and ease of formulation reasons.

It is believed that shorter EO chain nonionics suffer from the disadvantage of a reduced cloud point, whereas longer
20 EO chains lead to a surfactant which is difficult to formulate into a composition which dilutes to form a microemulsion phase.

25 Preferably, the nonionics have a monomodal distribution of EO chain lengths, i.e. mixtures of different ethoxylates are not preferred.

The amount of nonionic detergent active to be employed in the detergent composition of the invention will generally
30 be from 15 to 30%, preferably from 20 to 30% by weight.

It is preferred that the compositions are essentially free of anionic surfactants and preferably essentially free of
35 any charged surfactants. Preferably the level of anionic is below 2%wt of the level of nonionic surfactant present.

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Solvents

It is particularly preferred that the aqueous solubility should lie in the range 4-11%. Solubility can be
5 determined by experimental methods known to the skilled worker.

Solvents which have an aqueous solubility above 11%w/w in water, such as ethanol (miscible), 2-butanol (solubility
10 >20%), isopropyl alcohol (miscible), ethylene glycol derivatives (including butoxy ethanol [available as Butyl Cellosolve (TM)]: miscibility >20%), Butyl Digol (miscible) and diethylene glycol (miscible) do not give good results as the products become thin. It is preferred
15 that the compositions according to the invention are essentially free of these solvents.

The preferred alcoholic solvents include n-Butanol (soluble to 8%wt in water) and iso-butanol (soluble to
20 10%wt in water).

Relatively insoluble glycol ethers are particularly preferred. We have determined that excellent performance is attained when the solvent has a solubility in water of
25 from 5-10%. Solvents which are particularly preferred are those selected from the group comprising n-butoxy propanol (available as Dowanol PnB (RTM): soluble to 6%), di-propylene glycol monobutyl ether (available as Dowanol DPnB (RTM): soluble to 5%) and mixtures thereof.

Mixtures of solvents having an aqueous solubility in the range 4-11% with other, more highly water-soluble solvents having an aqueous solubility above 12% are not
30 excluded, but is preferred that the more highly water-soluble solvents are absent.
35

- 10 -

The preferred level of solvent lies in the range 8-15%wt on product.

5 Oils

For applications where the composition of the invention is intended to remove fatty soil it is believed that the oil must be a good solvent for fatty matter, especially those containing triglyceride. The rate at which any particular fatty soil dissolves in an oil can be simply determined by experiment.

These oils have a miscibility with water of less than 1% w/w.

Preferred oils are either:

- a) cyclic hydrocarbons having 6-15 carbon atoms, or,
- b) ethers of 2-6 carbon alcohols, or,
- c) mono-esters of 2-6 carbon fatty acids with 2-6 carbon alcohols,

wherein for (b) and (c) the total carbon number of the molecule is 6-10.

Preferred cyclic hydrocarbon oils are limonene and p-cymene. Preferred ethers include di-butyl ether. Preferred esters include butyl butyrate and amyl acetate. These are all hydrophobic liquids which can rapidly dissolve >20% of their own weight of triglyceride.

Longer chain esters such as ethyl decanoate are less preferred. These will dissolve sufficient quantity of fat

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but are believed to do so too slowly for effective cleaning.

5 Non-cyclic hydrocarbon oils such as dodecane and
hexadecane, and branched species such as citral (polar
acyclic terpene) and the ISOPAR (TM) series (branched
chain hydrocarbons) and water insoluble alcohols such as
n-decanol, which dissolve less than 15%w/w of fat over a
10 long period (several hours) and are considered less
suitable for use in those embodiments of the present
invention where fatty soil removal from hard surfaces is
important.

15 It is particularly preferred that the ratio between the
weight percentages of the solvent (c) and the oil (d) is
such that (c):(d) < 1.5:1. In the most preferred
embodiments of the invention the ratio is 0.9-0.4:1 as
solvent:oil. We have determined that the presence of
20 significantly larger quantities of solvent than oil leads
to a product which is not stable over a range of
temperatures or does not form a viscous lamellar phase.

For other applications the important properties of the oil
can extend beyond an ability to dissolve fatty soil. It
25 is envisaged that by choice of a suitable oil embodiments
of the invention might ensure delivery of a persistent
perfume a sunscreen or an insect repellent.

Typical levels of oil on product range from 6-18%wt,
30 levels of 8-16%wt are particularly preferred.

Minors

35 Various inessential components can be present in the
compositions of the present invention where these are

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adapted to particular uses. These optional components can be selected from the usual components employed such as perfumes, preservatives, colouring agents, antifoaming components, polymers, pH modifiers and the like, providing
5 that the composition retains its non-microemulsion form, of particle size >100nm when these components are added and can still be diluted to give a microemulsion.

The level of hydrotrope should preferably not exceed 2% of
10 the weight of nonionic surfactant present. More preferably, the level of hydrotrope should be lower than the amount effective to destabilise the lamellar phase as indicated by a removal of the property of birefringence from the neat product. Compositions according to the
15 present invention are preferably essentially free of hydrotropes. Hydrotropes include: aromatic sulphonates such as cumene, xylene and toluene sulphonate, urea, C1-C5 alcohols particularly ethanol and isopropyl alcohol, C2-C5 glycols, particularly ethylene glycol.

20 Particularly preferred compositions according to the present invention include:

a) 20-30%wt ethoxylated nonionic surfactant selected
25 from the group comprising: the condensation products ethylene oxide with aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration; the condensation products of ethylene oxide with alkylphenols whose alkyl group
30 contains from 6 to 12 carbon atoms; and mixtures thereof;

b) 8-13%wt of a solvent selected from the group
comprising: n-Butanol, iso-butanol, n-butoxy
35 propanol, di-propylene glycol monobutyl ether and mixtures thereof, and,

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c) 5-18%wt of an oil selected from the group comprising: limonene, para-cymene, di-butyl ether, butyl butyrate and mixtures thereof,

5 said compositions being essentially free of anionic surfactant, essentially free of hydrotrope and comprises a weight excess of oil(c) over solvent(b).

10 Preferred compositions according to the invention are clear and dilute to form clear solutions.

The invention will be described hereafter by way of example.

15

EXAMPLES

20 In order that the invention may be further understood it will be described hereafter with reference to embodiments of the invention and comparative examples.

25 In table 1, the 'NONIONIC' surfactant was Imbentin 91-35 OFA (RTM) a 5EO, 9-11 carbon alcohol ethoxylate. 'SOLVENT' was DOWANOL PnB (RTM, ex. DOW) and 'OIL' is limonene.

30

'Score (a)' is representative of extent of the spontaneous emulsification which the product exhibits on triglyceride samples on a glass microscope slide. Commercially available lard - 'Silver Cloud Fat' (TM) was spread onto the slide using a cotton bud to give a streaky but fairly uniform fat film. The glass slide was then mounted onto a microscope, a drop of test solution placed onto the fat film and the interaction between the liquor and the fat monitored over a few minutes at RT (no mechanical input).
35 The interaction could also be recorded by means of a video camera.

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Performance was scored on the following scale:

- | | | |
|----|---|--|
| | 1 | roll-up of fat but no removal, |
| 5 | 2 | roll-up of fat with minimal removal and/or emulsification, |
| | 3 | roll-up of fat with moderate and/or incomplete, removal and/or emulsification, |
| 10 | 4 | roll-up of fat with slow but complete removal and/or emulsification, and, |
| | 5 | roll-up of fat with rapid and complete removal and/or emulsification. |
| 15 | | |

'Score (b)' is representative of the extent of cleaning using a 'spot test', in which clean Decamel (RTM) tiles are sprayed with a model kitchen soil (a mix of triglycerides, fatty acid, clay and carbon) and allowed to stand at room temperature overnight before use. Alternatively, the soiled tiles were warmed in an oven at 70C for 10 minutes to increase soil adhesion to the tile and allowed to cool before use. Samples of liquors were applied to the soiled tiles at room temperature and the drops allowed to spread and remain in contact with the soil for about 20/30 seconds (up to about 4 minutes in the case of particularly ineffective solutions). The spots of liquid were then rinsed under the tap (hard water) or with a wash bottle (demin water). 'Spontaneous Cleaning' was assessed on the following scale according to the amount of visible soil remaining on the tile after rinsing.

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- 5 Excellent - complete soil removal,
- 4 Good - almost all soil removed,
- 5 3 Moderate - a spot with soil still visible but
which is markedly cleaner than the surroundings,
- 2 Poor - some soil removal,
- 10 1 Very poor - a very faint 'ring' at the edge of
the spot, and,
- 0 No soil removal.
- 15 Particle size was determined by use of a Malvern 4700 (TM)
photon correlation spectrophotometer using the method
given in the operating handbook.

20

Table 1

		1a	1b	1c	1d	1e	2a	2b	2c	2d
25	NONIONIC:	24	24	24	24	24	24	24	24	24
	SOLVENT:	10	10	10	20	-	8	8	8	8
	OIL:	12.5	12.5	12.5	-	-	16	16	16	16
	DILUTION:	1	8	16	1	1	1	4	8	16
30	Viscosity:	High	Low	Low	Low	Low	High	Low	Low	Low
	Score (a)	4	3	3	-	-	3	3	3	3
	Score (b)	5	-	-	0	0	5	5	5	5
35	Particle Size (nm):	>100	-	16	-	6	>100	20	17	16

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In the table, examples 1a and 2a are embodiments of the invention. Examples 1b and 1c illustrate the effects of diluting the composition of example 1a by factors of 8 and 16 respectively, whereas examples 2b, 2c and 2d illustrate the effects of dilution on the composition of example 2a by 4, 8 and 16 respectively. Examples 1d and 1e are comparative examples which demonstrate the cleaning behaviour of compositions which are similar to 1a but which have components absent.

From the table it can be seen that both examples 1a and 2a provide non-microemulsions, having a particle size above the 100nm limit. These compositions both exhibit bi-refringence. Upon dilution of the compositions of examples 1a and 2a, microemulsions are believed to be produced as the products obtained are thin, clear, have a particle size consistent with microemeulsions and do not exhibit bi-refingence. It can be seen, particularly from example 2, that cleaning performance is maintained at up to 16 times dilution.

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CLAIMS

1. An aqueous cleaning composition which upon aqueous
5 dilution by a factor of at least two produces a
stable microemulsion, said emulsion having a measured
dispersed phase particle size of 10-100 nanometeres,
said composition including:
- 10 a) 20-70wt% water,
- b) from 15-40wt% of a surfactant system comprising
at least one alkoxyated alcohol nonionic
15 surfactant and not more than 20wt% on surfactant
of anionic, cationic, amphoteric or zwitterionic
surfactant,
- c) from 5-30wt% of a solvent, said solvent having a
solubility of greater than 2%w/w but less than
20 12%w/w in water, and,
- d) 5-20wt% of a substantially water-insoluble oil,
said composition having a measured dispersed phase
25 particle size of greater than 100nm prior to
dilution.
2. Composition according to claim 1 comprising less than
2% anionic surfactant on total surfactant present.
- 30 3. Composition according to claim 1 wherein the solvent
has a solubility in water of from 5-10%.
4. Composition according to claim 1 wherein the solvent
35 is selected from the group comprising n-butoxy

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propanol, di-propylene glycol monobutyl ether, n-butanol, iso-butanol, and mixtures thereof.

- 5 5. Composition according to claim 1 wherein the oil is a hydrophobic liquid which can rapidly dissolve >20% of their own weight of triglyceride.
- 10 6. Composition according to claim 1 wherein the oil is selected from the group comprising limonene, para-cymene, di-butyl ether, butyl butyrate and mixtures thereof.
- 15 7. Cleaning composition according to claim 1 comprising:
- 20 a) 20-30%wt ethoxylated nonionic surfactant selected from the group comprising: the condensation products ethylene oxide with aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration; the condensation products of ethylene oxide with alkylphenols whose alkyl group contains from 6 to 12 carbon atoms; and mixtures thereof;
- 25 b) 8-13%wt of a solvent selected from the group comprising: n-Butanol, iso-butanol, n-butoxy propanol, di-propylene glycol monobutyl ether and mixtures thereof, and,
- 30 c) 5-18%wt of an oil selected from the group comprising: limonene, para-cymene, di-butyl ether, butyl butyrate and mixtures thereof,

35 said compositions being essentially free of anionic surfactant, essentially free of hydrotrope and comprises a weight excess of oil(c) over solvent(b).

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8. A process for cleaning a surface which comprises the step of treating the surface with a composition according to claim 1.

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/EP 95/02533

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/72 C11D3/18 C11D3/43 C11D3/20 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 418 986 (COLGATE-PALMOLIVE CO.) 27 March 1991 see page 3, line 51 - page 4, line 8; claims ---	1,2,4,8
P,A	US,A,5 419 848 (VANEENAM DONALD N.) 30 May 1995 see claims 1-5,13,14,17; examples 2,5,7 ---	1,3,4,7,8
A	US,A,4 511 488 (MATTA GRANT B.) 16 April 1985 cited in the application see the whole document --- -/--	1,4,6-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/EP 95/02533

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